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Modeling of Wide-Band-Gap Semiconductor Alloys and Related Topics

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Abstract:

This year's work was concerned with the electronic structure of ZnO and related alloys. The nature of the valence band fine structure was studied and progress made in identifying the problems underlying its identification by experimental optical studies. Valence band effective mass parameters were determined. The electronic structure of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys were studied, their bandgap bowing determined and their band offsets to ZnO and other related materials were investigated. The stability of MgO in the wurtzite structure relative to the rocksalt structure was investigated. A continuous transformation from rocksalt to wurtzite was discovered and applied both to MgO and to GaN.

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1 Introduction

This report describes research performed under grant no. N00014-98-1-0160 during the performance period Nov. 1998-Sept. 1999.

Within the general topic of modeling of alloys of wide-band-gap semiconductors, this year's work was focused on the wide band gap semiconductor ZnO and its related alloys with Mg, which have recently attracted considerable attention. The reasons for this renewed interest in ZnO are: 1) the increasing availability of large and high-quality bulk single crystals of ZnO by a variety of growth methods, including low-cost hydrothermal growth; 2) the recent demonstration of optically pumped stimulated emission, [1] 3) the development of epitaxial growth methods of ZnO and related $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys,[2] 4) the realization that ZnO is closely lattice matched to GaN but may be an interesting electrooptical material in its own right, surpassing GaN in certain aspects. The first International Workshop on ZnO was held in Dayton, Ohio, from October 7-8, 1999. The high quality of the crystals of ZnO is demonstrated among others by the possibility to obtain fine structure information on the valence band structure using photoluminescence.[3] This work has re-opened a 30-year old controversy over the ordering of the states near the valence band maximum. Our work described below was in part geared towards a better understanding of this controversy.

Our work has focused on two topics: 1) the valence band ordering and 2) the properties and stability of the alloys with MgO. Important progress has been made on both aspects and been presented already at some meetings. Some further work is necessary to bring these investigations to a definitive conclusion. Thus, a nocost extension was requested to continue this work.

We now briefly describe the progress made under each of these topics and then provide lists of presentations and publications obtained or in progress under this work.

2 Valence band structure

We here describe the problem of the valence band structure along with our specific calculations which provide progress towards its resolution.

The nature of the valence band maximum fine structure in ZnO was first studied by Thomas.[4] Based on the polarization dependence of the absorption and reflectivity spectra, he came to the conclusion that the valence band ordering of ZnO is inverted from the usual one in other II-VI wurtzite materials. Namely, the symmetry character of the highest valence band state (leading to the so-called A-exciton) according to his analysis was Γ_7 rather than Γ_9 . The symmetry of the B state would then be Γ_9 . The C-exciton also has symmetry Γ_7 . These splittings come about as a result of the interplay between spin-orbit coupling and crystal field splitting. His interpretation was that the crystal field splitting is large compared to the spin-orbit splitting. Without spin-orbit coupling, the valence band would be split into a singlet Γ_1 and a doublet Γ_5 . The singlet Γ_1 is essentially a p_z like state (with slight s -admixture) while the Γ_5 is a p_x, p_y like state. With the usual $\Gamma_5 > \Gamma_1$ ordering, one thus expects the C-exciton to be allowed in $\mathbf{E} \parallel \mathbf{c}$ polarization and the Γ_5 derived (unresolved A,B excitons) to be allowed for the other polarization $\mathbf{E} \perp \mathbf{c}$. This is essentially what was observed in Thomas's reflectivity spectra. Absorption reveals the fine structure splitting in A and B excitons. With the spin-orbit coupling present, the Γ_7 state derived from the Γ_5 will obtain a slight admixture of p_z while the Γ_9 stays purely x and y like. Thus, one expects the Γ_7 state to become weakly allowed for $\mathbf{E} \parallel \mathbf{c}$. Thomas's data revealed this to be the case for the highest energy A-exciton. Hence, his assignment. This was later confirmed also by Liang and Yoffe.[5]

On the other hand, the interpretation of the lines by Thomas was challenged by Park et al. [6] They concluded on the basis of temperature dependence studies and on the basis of a prior study by Reynolds et al.[7] that the lines which were identified as the A-exciton lines A_m and A_L (the latter being a longitudinal exciton) by Thomas, were, in fact, not arising from a free exciton but corresponded to the Γ_5 and Γ_6 states of a ionized donor bound exciton. This was later disputed by other authors, among them B. Segall,[8] who confirmed the free exciton nature of the absorption line in question by a study of the phonon assisted absorption onset. The controversy was never fully resolved, although most future papers adopted the interpretation of Thomas.

Recently, Reynolds et al. [3] were able to restudy this issue using second order photoluminescence spectra. The second order of the diffraction grating provided them higher resolution, fully resolving the additional fine structure of the excitons due to the exchange splitting. Furthermore, they studied the behavior of these spectra in a magnetic field. Their conclusion was that the line is indeed a free exciton line, but that nevertheless, the valence band maximum must have Γ_9 symmetry. We will discuss their arguments below in more detail.

The meaning of the ordering proposed by Thomas is that the spin-orbit splitting is negative. The possibility of a negative spin-orbit splitting was first suggested by Cardona in a study of copper and silver halides.[9] It was subsequently explained by Shindo.[10] The origin is the presence of lower lying d-bands. The valence band maximum being an antibonding combination of anion p-like states and cation d-like states, results in a negative contribution of the atomic d-orbitals to the effective spin-orbit splitting. Thus, one expects the possibility of a negative spin-orbit parameter if the d-bands lie fairly close to the valence band maximum and have a strong atomic spin-orbit parameter. This is clearly the case in Cu compounds. The situation is marginal in ZnO, because the d-bands here lie about 7 eV below the valence band maximum (according to photoemission data[11]). In previous work on nitrides, we already pointed out the importance of the d-bands in reducing the values of the spin-orbit splittings.[12]

From the above, it is clear that the results of a negative spin-orbit splitting may depend crucially on the position of the d-bands. Thus, we paid special attention to this feature in the band structures. Our initial band structure calculations, using the local density approximation (LDA) obtain a d-band position of about 5 eV below the VBM in contrast to the experimental value of 6.95 eV.[11] The sign of the spin-orbit splitting in this calculation was determined in two ways. First, in zincblende ZnO, the valence band splits into a 4-fold state of symmetry Γ_8 and a 2-fold state of symmetry Γ_7 . Thus simple inspection of the degeneracy of the eigenvalues revealed that Γ_7 was lying above Γ_8 , meaning a negative spin-orbit parameter. Secondly, inspection of the wave functions in the wurtzite case revealed that the highest valence band contained a p_z and s components, indicating Γ_7 symmetry while the second state had pure p_x, p_y (and some d-admixture) but absolutely zero p_z or s components. So, this means that in LDA, a negative spin-orbit splitting, confirming Thomas's conclusion is predicted.

However, one may argue that the LDA calculation places the Zn 3d band too high in energy and thus overestimates the negative component of the spin-orbit splitting. We thus further investigated the behavior of the splitting as a function of d-band position. These results are shown in Fig. 1 and Fig. 2. What we find is that both the crystal field and the spin-orbit splitting depend strongly on the d-band position. In fact, both decrease monotonically and nearly linearly as a function of increasing d-band binding energy. We find good agreement with the experimentally deduced $E_A - E_B$ and $E_B - E_C$ splittings for a d-band position of -6.25 eV. At the experimental d-band position, the crystal field splitting is strongly underestimated. How to explain this?

The origins of discrepancy between LDA and photoemission on the d-band position are twofold. First, there is the fact that LDA treats exchange and correlation in an orbital independent manner

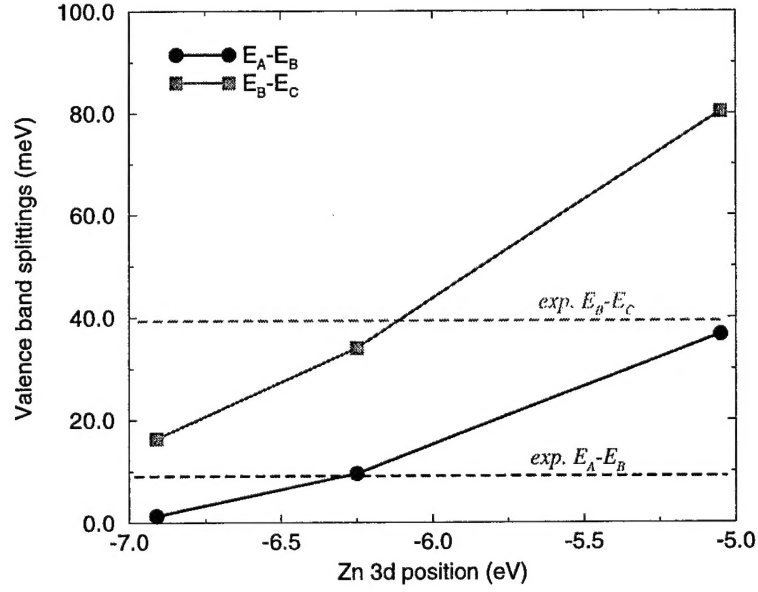


Figure 1: Valence band splittings versus d-band position in wurtzite ZnO

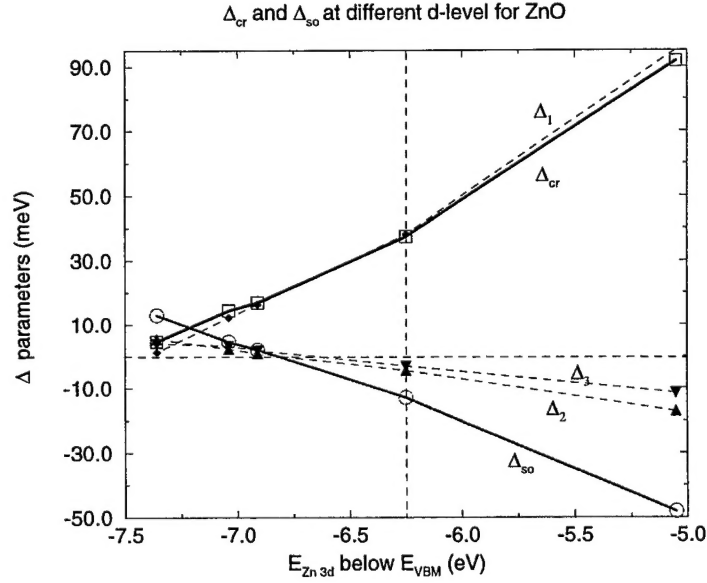


Figure 2: Crystal field ($\Delta_1 = \Delta_{cr}$ and spin-orbit splittings as function of Zn 3d band position: fits derived either with the quasicubic model using cubic $\Delta_{so} = 3\Delta_2 = 3\Delta_3$ or with the anisotropic spin orbit parameters Δ_2 and Δ_3 are shown.

and leads to a self-interaction error because of imperfect cancellation of the Coulomb and exchange integrals, in particular for localized states. Secondly, however, in the photoemission experiment, a final state relaxation effect is involved. In some sense, in order to obtain the correct valence band splitting we need to include the first but not the second effect.

Another way of phrasing this is within the language of quasiparticle theory. The energy of a state as determined by photoemission is the quasiparticle energy, which follows from an equation which contains a non-local and energy dependent self-energy operator instead of a exchange and correlation potential. This self energy operator in the GW approximation is essentially like a dynamically screened Hartree Fock exchange term. The energy dependence of this term implies that there is strictly no hope of obtaining both the valence band maximum and the d-band states from the diagonalization of one energy independent Hamiltonian matrix. On the other hand, let's assume we make a static approximation to the screening of the exchange. In that case, we will already correct the self interaction effect that LDA gets wrong and obtain a much better orbital dependent treatment of exchange. Essentially, this will lead to a downward shift of the d-band. This is what our calculation is simulating in a simple manner. We simply shift the d-band atomic orbital energy or diagonal matrix element in our LMTO representation of the Hamiltonian. Clearly, following the above argument we should not expect that we get the d-band and VBM correct with the same shift. Thus, since we are here interested in the VBM, we adopt a slightly empirical point of view and use this shift as an adoptable parameter. The result that we obtain a d-band position intermediate between the LDA value and the experimental value for the correct VBM splitting is completely in agreement with expectations of the above outlined theory. Of course, a further ab-initio justification of the d-band shift required would be preferable and will be investigated in future work. We have in fact hopes that this can be accomplished within the frame work of recently proposed screened exchange Generalized Kohn Sham methods.[13] For the moment, however, let us be satisfied that indeed both the $E_A - E_B$ and $E_B - E_C$ splittings can simultaneously be fitted with one empirical d-band shift parameter.

Now, we can with this shift examine again the symmetry of the VBM states. We find, we still have Γ_7 symmetry for the VBM. Also, if we use the same shift of the d-band in zincblende, we still find the doublet above the quartet. Finally, Fig. 2 shows that assuming a negative spin orbit splitting at this d-band position leads to the expected nearly linear dependence vs. the d-band position, whereas assuming a positive splitting, would lead to a nonmonotonic behavior. Clearly, we can easily identify the point where the spin-orbit splitting passes through zero as a function of d-band position. Furthermore, we note that if we shifted the d-band to the point where the spin-orbit splitting becomes positive, the crystal field splitting would be strongly underestimated. Further corrections beyond LDA would be expected to perhaps reduce this splitting but not to increase it. In fact, the gap is still underestimated and including a gap shift will reduce the interaction of the Γ_1 with the conduction band and thus reduce the crystal field splitting. This effect is expected to be small. We note finally that with this d-band shift, the gap correction required for ZnO is similar to that in GaN. This is expected because the two materials have nearly the same experimental gap, as well as close correspondence in lattice constant, density of electrons, dielectric constant, all factors which influence the GW corrections.

So, in summary, there is no doubt that the calculation leads to a negative spin-orbit splitting even in a model that goes beyond LDA by including the expected shifts of the d-band and their influence on the crystal field, spin-orbit splitting and gap correction.

It then remains to discuss the discrepancy with the recent conclusions by Reynolds et al. [3] To that end we must first realize that their conclusion is indirect because it is based on the behavior of excitons rather than of the valence bands directly. That is, one might have that the exciton binding

energy of the A, B and C, derived excitons is sufficiently different that the ordering of the exciton bands differs from that of the valence bands. In fact, one may not even strictly speak of B, and C derived excitons, because the exciton binding energy is of order 60 meV while the A-B splitting is only 9.5 meV. This problem was already mentioned in the theory paper by Hopfield [14] accompanying the Thomas paper. This aspect deserves further investigation. A theory for dealing with these aspects is available through Baldereschi and Lipari's work[15] but implementation of it for wurtzite remains to be accomplished. We hope to address this in future work.

Another explanation of the discrepancy however is possible. While there is of course no question about the validity of the data of Reynolds et al., their assignment of the features to the symmetry should be carefully examined. When one considers the excitons formed by a Γ_7 valence band and a Γ_7 conduction band, three possible symmetries are obtained: Γ_1 , Γ_2 and Γ_5 . When, considering a Γ_9 valence band, the possible symmetries of the exciton are: Γ_5 and Γ_6 . In short:

$$\begin{aligned}\Gamma_7 \otimes \Gamma_7 &= \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 \\ \Gamma_9 \otimes \Gamma_7 &= \Gamma_6 \oplus \Gamma_5.\end{aligned}$$

Now, Γ_5 is allowed strictly speaking only for $\mathbf{E} \perp \mathbf{c}$ and Γ_1 is allowed for $\mathbf{E} \parallel \mathbf{c}$. The other lines are forbidden but may still be weakly visible because of not exact k-conservation, or because of not perfect alignment of the beams vs. the crystal axis. The argument of Reynolds et al.[3] is primarily based on the behavior of PL lines in a magnetic field. What one finds is a low energy line at 3.375 eV which exhibits a strong splitting in a magnetic field and a higher energy line at 3.373 eV with negligible splitting. They assign the strongly split line to Γ_6 because one expects for Γ_6 a g-factor which is the sum of the electron and hole g-factors. This then leads to the Γ_9 assignment of the A-exciton. Their g-factors obtained are in agreement with those extracted from shallow neutral donor bound excitons for the holes and with the known electron g-factor. It is somewhat difficult to explain in their interpretation why the forbidden Γ_6 line is almost as strong as Γ_5 for the $\mathbf{E} \parallel \mathbf{c}$ polarization but not for the $\mathbf{E} \perp \mathbf{c}$ polarization, although one might in luminescence invoke a thermal Boltzmann factor favoring the low energy state. At 2K the Boltzmann factor $\exp(-\Delta E/kT)$ for $\Delta E \approx 2$ meV is about a factor 12.

On the other hand, there is no reason why the g-factor for the bound exciton should equal that of the free exciton, and in fact, the g-factor for the holes could well be negative. A negative g-factor was reported previously for ZnO by Blattner et al. [16] and was recently also reported for the Γ_7 hole in GaN by Campo et al. [17]. In that case, an alternative interpretation of the strongly split line in magnetic field is that these represent the Γ_1 and Γ_2 lines. The Γ_2 is forbidden without magnetic field but becomes allowed in a magnetic field because the latter has the symmetry Γ_2 . The two states then couple and repel each other resulting in splitting. In that case, the Γ_5 derived from two Γ_7 's should split as the sum of the g-factors while the $\Gamma_1 - \Gamma_2$ splitting will behave as the difference. So, if the Γ_7 hole g-factor is negative, the spectrum can alternatively be interpreted as being derived from a Γ_7 VBM. In fact, this interpretation of the Zeeman splitting was already suggested by Thomas. His Zeeman study was done on absorption rather than PL lines and with less resolution but the essentials stay the same. One might ask with this interpretation why the Γ_1 is so weak compared to Γ_5 for $\mathbf{E} \parallel \mathbf{c}$? However, it should be kept in mind that this state still is primarily *x, y*-like with only a very small *z* admixture because the crystal field splitting is much larger than the spin-orbit splitting. So, even with a Boltzmann factor advantage, it may be quite weak.

In any case, our conclusion from this whole analysis is that a crucial piece of missing information is an independent determination of the sign of the g-factor. Thus, we have initiated work to calculate

Table 1: Rashba-Sheika-Pikus parameters* for ZnO valence band effective Hamiltonian

A_1	A_2	A_3	A_4	A_5	A_6	A_7	Δ_{cr}	Δ_{so}
-3.78	-0.44	3.45	-1.63	1.68	-2.23	0.025	38	-13

* The A_i parameters are in units of $\hbar/2m_e$ for $i=1\dots 6$ and $e^2/2$ for A_7 , Δ_{cr} and Δ_{so} are in meV.

Spin orbit splitting		
$\Delta_{so}/3$	Δ_2	Δ_3
-4.33	-4.53	-3.05

the g-factor directly from our first-principles band structures using perturbation theory. We hope to finish this work during the requested nocost extension.

In summary, the controversy of the valence band ordering revolves around the sign of the spin-orbit splitting, which depends sensitively on the Zn d-band position. Our calculations including considerations beyond LDA strongly favors a negative spin orbit splitting. This disagrees with the current interpretation in the literature of the photoluminescence Zeeman splittings. However, the latter is based essentially on an assumption about the sign of the hole g-factor which for free holes has not been determined independently. An alternative explanation reconciling the theory with the experiment is possible if the hole g-factor of this particular valence band is negative. Work is in progress to determine the sign of the hole g-factor. Another possible reconciliation between theory and experiment is that the assignment as a Γ_5 and Γ_6 exciton would be correct but that this exciton ordering cannot be directly equated to the valence band ordering because of the intermixing of excitons derived from different valence band states. Such intermixing is to be expected because of the small band splitting compared to the the large exciton binding energy. This aspect of the problem requires further investigation. An unraveling of this problem in conjunction with Reynold's data will further provide information on the exciton exchange coupling paramter.

Finally, we note that similar questions recently have appeared for GaN. The fine splittins due to the exchange interaction of excitons have recently been observed in GaN. In GaN, as in ZnO, the binding energy of the excitons is comparable and exceeds the valence band splittings. hence an explicit inclusion of the exciton intermixing effects must be included before conclusions on the valence band splittings can be drawn. This may in part help to resolve the discrepancies between current LDA theory for the crystal field splitting and the values deduced from experiment. We plan also to reinvestiage the effects of the Ga d-bands in view of what we have learned from the study of ZnO.

As part of this work, we will have obtain the valence band effective Hamiltonian mass parameters. in ZnO. Our present best set of parameters for the Rashba-Sheika-Pikus Hamiltonian, described e.g. in ref. [18] are given in Table 2.

3 $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

Our first model of the band gap bowing in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy system is based on calculations for zincblende based structures. In particular, we used a 50% ZnO, MgO structure and the end compounds. In this model, the residual strain in the alloy is taken into account by considering the expected bondlengths of Zn-O and Mg-O based on a Keating model for the dilute limits. This method

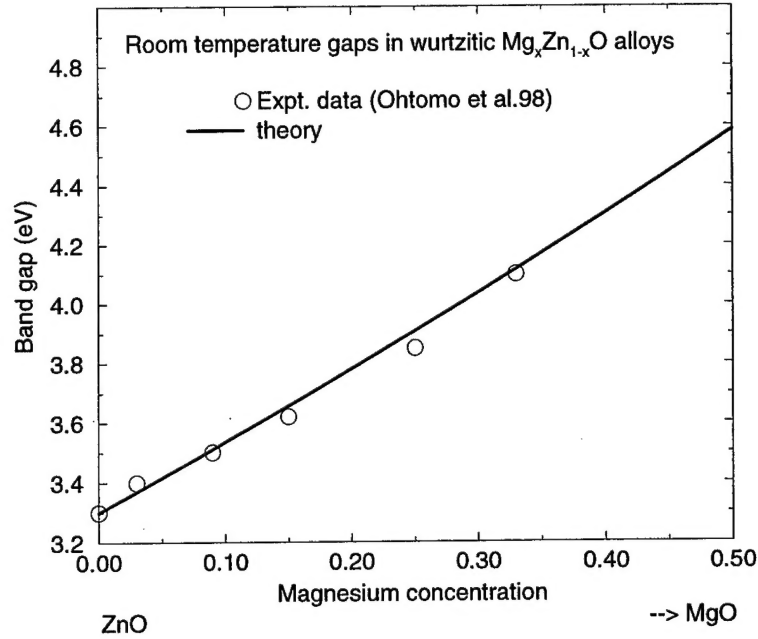


Figure 3: Band gaps in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys.

was developed in earlier work under this grant and is explained in detail in Ref. [19]. From a statistical treatment, the band gap bowing is then estimated for zincblende ZnMgO . It is found to be 0.56 eV. Determining the band gaps of the end compounds is not trivial because MgO has naturally rocksalt structure. We calculated the band structure in the rocksalt, wurtzite, relaxed wurtzite (see below) and zincblende structures. We calculated ZnO in the wurtzite and zincblende structures. All of these calculations were in the LDA. From the known experimental gap in rocksalt and assuming the correction to be independent of structure, we then obtain an estimated band gap of wurtzitic MgO . Along with the experimental ZnO gap and the bowing coefficient, this provides the calculated data for the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys shown in Fig. 3. In spite of the numerous assumptions this calculation is in excellent agreement with the data by Ohtomo et al. [2].

Although these alloys have been successfully grown up to about 40 %, they were found in annealing studies to be only stable towards phase separation up to about 15 %.[20] Also, from the theory point of view, many precautions are in order. To further investigate the stability of the alloys in wurtzitic vs. rocksalt structure and the effects of local relaxation on the bowing, we started with an investigation of the stability of the end compound MgO .

To our surprise, what we found is that the MgO wurtzite structure is not stable at all. In fact, restricting the structure to wurtzite symmetry, the u parameter which gives the ratio of the bond length in the c -direction to the c lattice constant, was found to relax to a value of 1/2. What this implies is that the structure obtains an additional mirror symmetry and degenerates into the h-BN structure. This structure is still hexagonal but now the O atoms above and below Mg are at equal distance and the buckling of the hexagonal network is wiped out. The hexagonal honeycomb layers become completely flat. Typically in h-BN the interplanar distance is much larger than the in-plane distance, resulting in effectively 3-fold coordination typically of π -bonding in graphite. However,

here the bonds in the c -direction are about the same as in the plane. This means that Mg is roughly 5-fold coordinated instead of 4-fold. This can be understood by the preference of ionic materials for high coordination. Within the restrictions of hexagonal symmetry this is the best MgO can do. It was then discovered that a further in-plane deformation changes the structure to rocksalt. Changing the b/a ratio where b refers to the distance $\sqrt{3}a$ in the $[1200]$ direction to a will turn the rectangular 2×1 projected cell into a square projected cell of the rocksalt. The energy as a function of the transformations is shown in Fig. 4.

The structures are shown in Fig. 5.

We see that the h-BN structure has a metastable region only. This discovery of a continuous path of transformation between wurtzite and rocksalt prompted us to investigate the same transformation in GaN. In fact, in GaN, and other nitrides, a transformation from wurtzite to rocksalt has been observed at high pressures. The energy landscape for this transformation with a plausible transformation path is shown in Fig. 6 as a contour plot. It shows that the rocksalt structure has to overcome a barrier to transform back to wurtzite. Note again that in MgO the situation is inverted: rocksalt is the stable structure, wurtzite is unstable.

This raises serious questions on how the structure will locally relax around Mg atoms in ZnMgO alloys. This question is now under further investigation.

Further details on the rocksalt to wurtzite transformation will be given in a paper that is currently in preparation.

Another important parameter for the use of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys as barrier material along with ZnO quantum wells is the band offset. We found that the band offset is almost entirely in the conduction band. This was confirmed by data of Ohtomo et al. [20] who found a ratio of $\Delta E_v/\delta E_c \approx 1/9$. This means that electrons will have good confinement but holes will not. In view of this unfavorable result, we have also investigated some other possible barrier materials and their band offsets to ZnO. Among these an interesting candidate is LiGaO_2 , a material closely related in structure to ZnO. All these band offset calculations were performed in the simple dielectric midgap model and require refinement to take in to consideration the specific strains in lattice mismatched situation and the specific interface orientations. However, they are known to provide at least initial guidance for other semiconductor materials. Our calculated band offsets are shown in Fig. 7

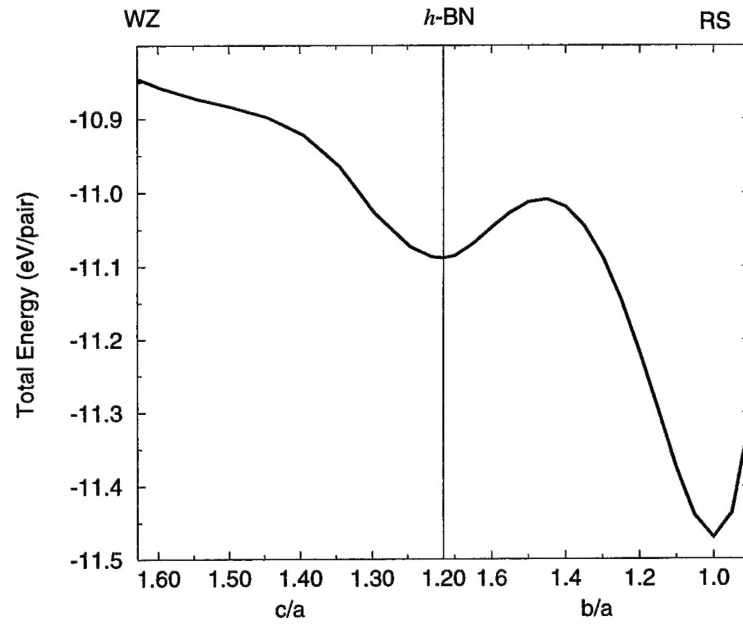


Figure 4: Total energy of MgO under the wurtzite to h-BN and h-BN to rocksalt continuous transformation. The volume and the internal structural parameters are relaxed for each c/a or b/a ratio.

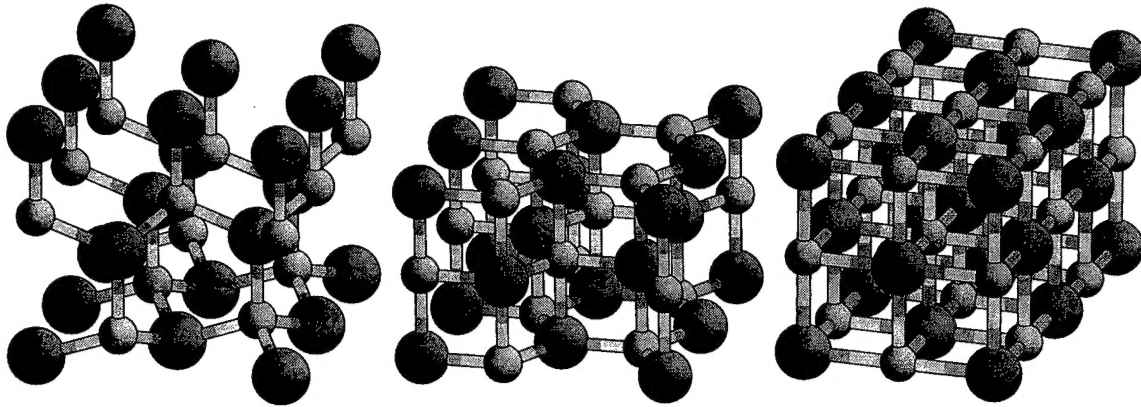


Figure 5: From left to right, ideal wurtzite structure, h-BN structure (or wurtzite with $u = 1/2$) with bond length ratios corresponding to the metastable structure of MgO, and rocksalt structure.

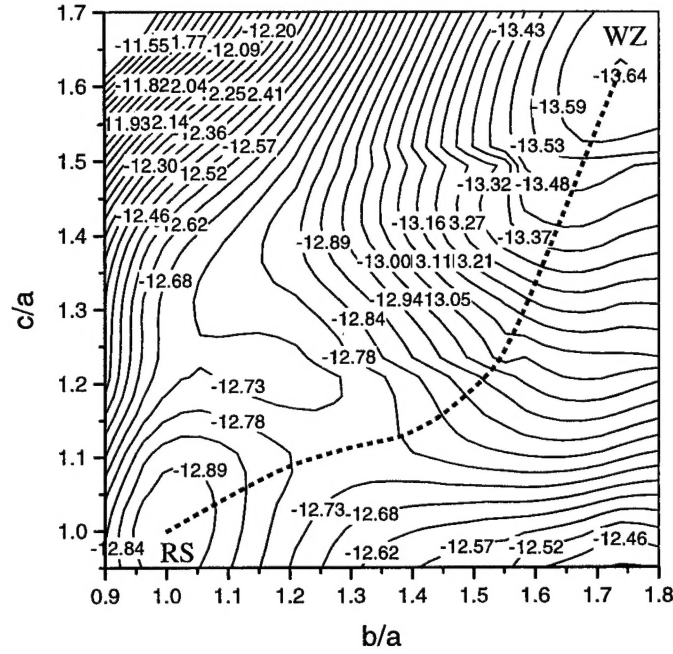


Figure 6: Total energy of GaN as function of c/a and b/a parameters, as defined in text with relaxed volume and internal parameters.

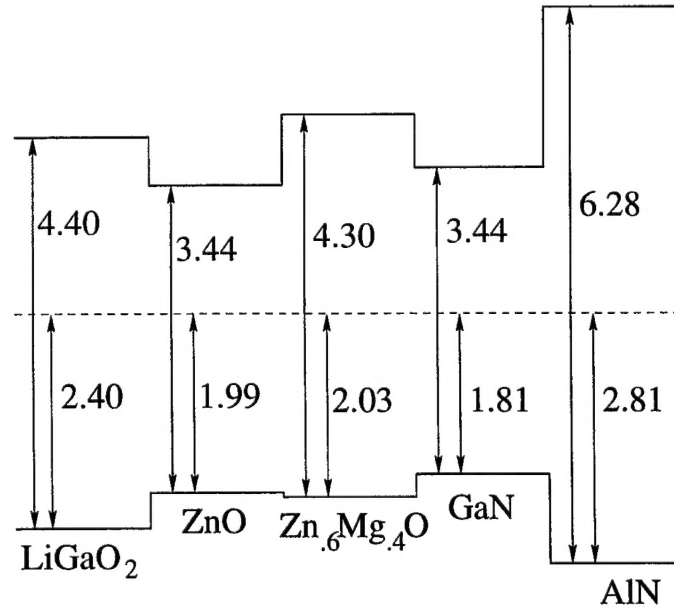


Figure 7: Band-sets between ZnO and related materials. The dashed line gives the dielectric midgap point with respect to which the band structures are aligned.

4 Publications and reports.

The following papers were published or are in preparation.

1. W. R. L. Lambrecht, S. Limpijumnong, and B. Segall, Theoretical studies of ZnO and related $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys, in *GaN and Related Alloys*, edited by Stephen J. Pearton, Chhping Kuo, Alan F. Wright, Takeshi Uenoyama, Mater. Res. Soc. Symp. Vol. 537, p. G6.8, also appearing in MRS Internet J. Nitride Semicond. Rese 4S1 G6.8 (1999).
2. H. Morkoç, R. Congolani, W. Lambrecht, B. Gil, H-X. Jiang, J. Lin, D. Pavlidis, and K. Shenai, Material Properties of GaN in the Context of Electron Devices, in *GaN and Related Alloys*, edited by Stephen J. Pearton, Chhping Kuo, Alan F. Wright, Takeshi Uenoyama, Mater. Res. Soc. Symp. Vol. 537, p. G1.21, also appearing in MRS Internet J. Nitride Semicond. Rese 4S1 G1.2.1 (1999).
3. Theoretical study of wurtzite to rocksalt transformation in MgO and GaN, in preparation for Phys. Rev. B

The following presentations were given at conferences.

1. MRS Fall meeting 1999, poster G6.8 in Symposium S4.1
2. APS March Meeting
3. First International ZnO workshop in Dayton, OH, October 7-8, 1999

Other activities during this period. The PI during this period also was co-author on a paper with Morkoç et al. relating to the piezoelectric and spontaneous polarization effects in the nitrides and their impact on devices.

He also consulted on a paper on the electronic transport in ZnO through a collaboration with P. P. Ruden and J. D. Albrecht at the University of Minnesota. The important result of this work is that ZnO has a higher drift velocities at high fields than GaN and that this is due to the difference in energy from the conduction band to the first secondary value being larger in ZnO than in GaN. The work was mainly carried out at Univ. Minnesota but was based on the band structure calculations in our group at CWRU.

This resulted in a paper submitted to J. Appl. Phys. "High field electron transport properties of bulk ZnO," J. D. Albrecht, P. P. Ruden, S. Limpijumnong, W. R. L. Lambrecht, and K. F. Brennan

The graduate student Sukit Limpijumnong involved in the work on ZnO presented his Ph.D thesis in June 1999 with work on SiC polytypes. The present grant has contributed to his support during this period.

References

- [1] D. C. Reynolds, D. C. Look, and B. Jogai, Solid State Communn. **99**, 873 (1996), "Optically pumped ultraviolet lasing from ZnO"
- [2] A. Ohtomo, M. Kawasaki, T. Koida, K. Masubichi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **72**, 2466 (1998), " $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ as a II-VI widegap semiconductor alloy."

- [3] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. cantwell and W. C. Harsh, Phys. Rev. B **60**, 2340 (1999) "Valence-band ordering in ZnO."
- [4] D. G. Thomas, J. Phys. Chem. **15**, 86 (1960), "The exciton spectrum of Zinc Oxide."
- [5] W. Y. Liang and A. D. Yoffe, Phys. Rev. Lett. **20**, 59 (1968), "Transmission spectra of ZnO single crystals."
- [6] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966), "Exciton spectrum of ZnO."
- [7] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **140**, A 1726 (1965), "Zeeman Effects in the Edge Emission and Absorption of ZnO."
- [8] B. Segall, Phys. Rev. **163**, 769 (1967), "Intrinsic Absorption "Edge" in II-VI Semiconducting Compounds with the Wurtzite Structure."
- [9] M. Cardona, Phys. Rev. **129**, 69 (1963), "Optical properties of the Silve and Cuprous Halides."
- [10] K. Shindo, A. Morita, and H. Kamimura, J. Phys. Soc. Japan. **20**, 2054 (1965), "Spin-orbit Coupling in Ionic Crystals with Zincblende and Wurtzite Structures."
- [11] R. T. Girard, O. Tjernberg, G. Chiaia, S. Söderholm, U. O. Karsson, C. Wigren, H. Nylén, and I. Lindau, Surf. Sci. **373**, 409 (1997), "Electronic structure of ZnO (0001) studied by angle-resolved photoelectron spectroscopy."
- [12] W. R. L. Lambrecht, K. Kim, S. N. Rashkeev, and B. Segall, "Electronic and Optical Properties of the Group-III Nitrides, their Heterostructures and Alloys," in *Gallium Nitride and Related Materials*, edited by R. D. Dupuis, F. A. Ponce, S. Nakamura, and J. A. Edmond, Mater. Res. Society Symp. Proceedings Vol. 395, (MRS, Pittsburgh 1996), p.455
- [13] A. Seidl, A. Görling, P. Volg, J. A. Majewski, M. Levy, Phys. Rev. B **53**, 3764 (1996), "Generalized Kohn-Sham schemes and the band-gap problem."
- [14] J. J. Hopfield, Phys. Chem Solids. **15**, 97 (1960), "Fine structure in the optical absorption edge of anisotropic crystals."
- [15] A. Baldereschi and N. O. lipari, Phys. Rev. B **3**, 439 (1971), "Energy levels of Direct Excitons in Semiconductors with Degenerate Bands."
- [16] G. Blattner, G. Kurtze, G. Schmieder, and C. Klingshirn, Phys. Rev. B **25**, 7413 (1982), "Influence of magnetic fields up to 20 T on excitons and polaritons in CdS and ZnO."
- [17] J. Campo, M. Julier, D. Coquillat, J. P. Lascaray, D. Scalbert, and O. Briot, Phys. rev. B **56**, R7108 (1997), "Zeeman splittings of excitonic transitions at the Γ point in wurtzite GaN: a magnetorefectance investigation."
- [18] K. Kim, W. R. L. Lambrecht, B. Segall, M. van Schilfgaarde, Phys. Rev. B **56**, **56**, 7363-7375 (1997) "Effective masses and valence-band splittings in GaN and AlN."
- [19] Kwisn Kim, Ph.D. thesis, Case Western Reserve Univeristy, 1998.
- [20] A. Ohtomo, private communication.

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